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*Published in:*  
Journal of Physics%3A Condensed Matter

*DOI:*  
[10.1088/0953-8984/3/41/010](https://doi.org/10.1088/0953-8984/3/41/010)

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*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
1991

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Loosdrecht, P. H. M. V., & Janner, A. (1991). A Raman and FIR spectroscopic study of the solid solution  $(\text{N}(\text{CH}_3)_4)_2\text{ZnCl}_4\text{-xBr}_x$ . *Journal of Physics%3A Condensed Matter*, 3(41). <https://doi.org/10.1088/0953-8984/3/41/010>

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## A Raman and FIR spectroscopic study of the solid solution $(\text{N}(\text{CH}_3)_4)_2\text{ZnCl}_{4-x}\text{Br}_x$

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Received 19 March 1991, in final form 31 May 1991

**Abstract.** Polarized Raman and far-infrared spectra ( $10\text{--}350\text{ cm}^{-1}$ ) of the solid solution  $(\text{N}(\text{CH}_3)_4)_2\text{ZnCl}_{4-x}\text{Br}_x$  are presented for several compositions ( $x = 0, 1, 2, 2.9$  and  $4$ ) in the high- ( $300\text{ K}$ ) and low- ( $60\text{ K}$ ) temperature phases of the crystals. Apart from the internal modes of the  $\text{ZnCl}_4^{2-}$  and  $\text{ZnBr}_4^{2-}$  ions, several new active internal modes are found in the spectra, originating from the mixed  $(\text{ZnCl}_{4-n}\text{Br}_n)^{2-}$  ions ( $n = 1, 2, 3$  and  $4$ ). The spectra are in fair agreement with a simple 'free' ion model for the vibrational modes of the  $(\text{ZnCl}_{4-n}\text{Br}_n)^{2-}$  ions. From the intensities of the tetrahedral  $\nu_1$  modes, the relative concentrations of the various  $(\text{ZnCl}_{4-n}\text{Br}_n)^{2-}$  ions in the crystals are estimated. Using these relative concentrations the value of  $x$  in the crystals is calculated, and found to be in good agreement with the stoichiometries of the crystal growth solutions. A pronounced low-frequency mode is observed in the spectra which scales with the average moment of inertia of the  $(\text{ZnCl}_{4-n}\text{Br}_n)^{2-}$  ions, and is therefore assigned to a librational mode of these ions.

### 1. Introduction

The solid solution  $(\text{N}(\text{CH}_3)_4)_2\text{ZnCl}_{4-x}\text{Br}_x$  belongs to the  $\text{A}_2\text{BX}_4$  family of dielectrics, having in general an orthorhombic ( $\beta\text{-K}_2\text{SeO}_4$ ) high-temperature phase. At lower temperature, different sequences of modulated phases are found for the members of this family, among which an incommensurate one is often found. The many common structural features among the members leads to the assumption that the modulation in this family has a common origin (Janssen 1986, Godefroy 1987). In fact, for many members the phases (both commensurate and incommensurate) can be described to a very good approximation as different three-dimensional intersections of a four-dimensional structure, with a single superspace group symmetry (the prototype symmetry group).

A few years ago, Colla *et al* (1984) determined the  $x$ - $T$  phase diagram of the solid solution  $(\text{N}(\text{CH}_3)_4)_2\text{ZnCl}_{4-x}\text{Br}_x$  (tetramethylammonium-tetra(chloro,bromo)zincate, hereafter denoted by TZCB). They found a rich variety of phases and phase transitions. The phase transitions in this system result mainly from modulated rotations  $(\theta_x, 0, \theta_z)$  and translations  $(0, t_y, 0)$  of the  $\text{N}(\text{CH}_3)_4^+$  and of the  $(\text{ZnCl}_{4-n}\text{Br}_n)^{2-}$  (hereafter denoted by  $\text{ZCB}_n^{2-}$ ) tetrahedra. At high temperature ( $T > 293\text{ K}$ ) the phase has space group symmetry  $Pnma$  for all compositions. At lower temperature the pure

chloride compound exhibits phase transitions (Sawada *et al* 1978) to respectively an incommensurate phase, an orthorhombic, two monoclinic and finally an orthorhombic phase again. The pure bromide compound, however, only exhibits one phase transition to a monoclinic low-temperature phase (Gesi 1982, Trouelan *et al* 1985). The modulated incommensurate phase present in the  $x = 0$  compound disappears at  $x \approx 3$ . Near  $x \approx 3$ , the wavevector of the modulation continuously changes from an incommensurate to a commensurate value. Indeed, this is exceptional, as usually one observes a discontinuous jump of the order of  $10^{-2}$  to the rational value in the modulation parameter. The continuity of the modulation parameter is interesting in view of a possible additional electromagnetic propagation mode in incommensurate structures with a nearly commensurate modulation, as predicted by van Beest (1986).

The purpose of the present paper is to obtain a better insight into the basic vibrational properties of TZCB. In order to study these properties we have performed Raman and far-infrared (FIR) spectroscopic experiments on several solid solutions in their high- and low-temperature phases. An extensive Raman investigation of the pure Cl compound has already been performed by Meekes *et al* (1988). We have concentrated our attention on the region of  $ZCB_n^{2-}$  vibrational modes, not only because of their relation to the phase transitions in this material, but also in order to obtain a better understanding of the distribution of Cl and Br in this system. The Cl,Br distribution is expected to influence both the selection rules and the intensities in Raman and FIR experiments, as will be shown in sections 3 and 4.

This paper is organized as follows. In section 2 the experiments are described and the resulting spectra are presented. The activity of the internal  $ZCB_n^{2-}$  modes is discussed in terms of the free tetrahedral ion symmetry modes in section 3. In section 4 the spectra presented in section 2 are discussed. Finally, in section 5 some conclusions are given.

## 2. Experimental procedure

The crystals used in the experiments are grown from a seed in an aqueous solution of a stoichiometric mixture of  $(N(CH_3)_4)Y$  and  $ZnY_2$  ( $Y = Cl, Br$ ) by a slow convection method (Arend *et al* 1986). In this way, optically transparent crystals ( $\sim 1 \text{ cm}^3$ ) were obtained from a solution with a known bromide concentration ( $x$ ). The actual Br concentration is expected to be somewhat higher than this value. The crystals are oriented using their rich morphology (Dam and Janner 1986, Vogels 1990). The unit-cell dimensions for a crystal with  $x = 2.9$  are determined by x-ray diffraction to be  $a = 12.49 \text{ \AA}$ ,  $b = 9.24 \text{ \AA}$  and  $c = 15.90 \text{ \AA}$ , which is consistent with the results of Arend *et al* (1986).

For the polarized Raman experiments, the crystals are cut and polished to platelets (dimension  $\sim 2 \times 3 \text{ mm}^2$ , 0.5–1 mm thick). The platelets are mounted in an Oxford cryostat (temperature stabilization better than 1 K). The Raman spectra are recorded in a standard way ( $90^\circ$  geometry) using the 514.5 nm line of an  $Ar^+$  laser (unfocused, power  $< 250 \text{ mW}$ ) as the exciting source.

The TZCB crystals have a strong absorption in the FIR region, making it very difficult to measure the absorption directly on single crystals. In order to be able to obtain FIR absorption spectra, we have therefore powdered the crystals and embedded them in a polyethylene platelet ( $\sim 0.35 \text{ mm}$  thick). In this way, samples are obtained with a known low molar concentration of the crystal ( $\sim 5\%$ ). The unpolarized

FIR transmission spectra were measured at room temperature using a Bruker FT-IR spectrometer.

### 2.1. FIR experiments

FIR transmission spectra of the powdered samples embedded in a polyethylene matrix were measured relative to the transmission of pure polyethylene. Some typical spectra at room temperature for  $x = 0, 1, 2.9$  and  $4$  are shown in figure 1. As  $x$  increases some modes shift in frequency and new modes appear in the spectra, although the modes of the mixed tetrahedra are not resolved in this case. The structure at  $456\text{ cm}^{-1}$  present in all spectra is due to the tetrahedral  $\nu_4$  symmetry modes of the  $N(CH_3)_4^+$  ions (Edsall 1937). The  $\nu_3$  and  $\nu_4$  modes of  $ZnCl_4^{2-}$  and  $ZnBr_4^{2-}$  are clearly visible as broad absorption lines in the spectra.

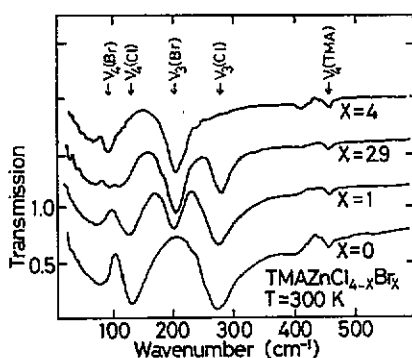


Figure 1. Room temperature FIR transmission spectra of powdered TZCB crystals ( $x = 0, 1, 2.9$  and  $4$ ) embedded in a polyethylene matrix. A pure polyethylene sample has been taken as a reference.

### 2.2. Raman experiments

Polarized Raman spectra are measured for  $x = 0, 1, 2, 2.9$  and  $4$  in the high- and low-temperature phases. As already mentioned, we focused on the frequency range of the internal  $ZCB_n^{2-}$  modes  $\nu_1, \dots, \nu_4$  ( $10\text{--}350\text{ cm}^{-1}$ ) (Morris *et al* 1963). There are two regions of interest in the spectra. The first one ( $10\text{--}150\text{ cm}^{-1}$ ) contains the external modes and the  $\nu_2$  and  $\nu_4$  internal  $ZCB_n^{2-}$  modes, whereas the second one ( $150\text{--}350\text{ cm}^{-1}$ ) contains the  $\nu_1$  and  $\nu_3$  internal modes of the  $ZCB_n^{2-}$  tetrahedra. The internal modes of the  $N(CH_3)_4^+$  ions lie at higher frequencies (Edsall 1937). The results of the Raman experiments can be found in figure 2(a) ( $T = 300\text{ K}$ ) and 2(b) ( $T \approx 60\text{ K}$ ). Raman spectra of different crystals are generally difficult to compare quantitatively due to the variations of for instance the optical quality of the samples. In order to get a better quantitative comparison of the spectra, we have therefore normalized the spectra of the crystals with a different composition in figure 2(a) and 2(b) with respect to the integrated intensity of the  $150\text{--}350\text{ cm}^{-1}$  region in  $A_g$  geometry of the same crystal, thereby assuming that the scattering efficiency of the  $ZCB_n^{2-}$  tetrahedra is approximately the same for all  $n$ .

In the monoclinic low-temperature phases, domains differing in monoclinic angle, and a rotation of the indicatrix around the unique axis are observed under a polarization microscope. Due to the rotation of the indicatrix, light polarized along one

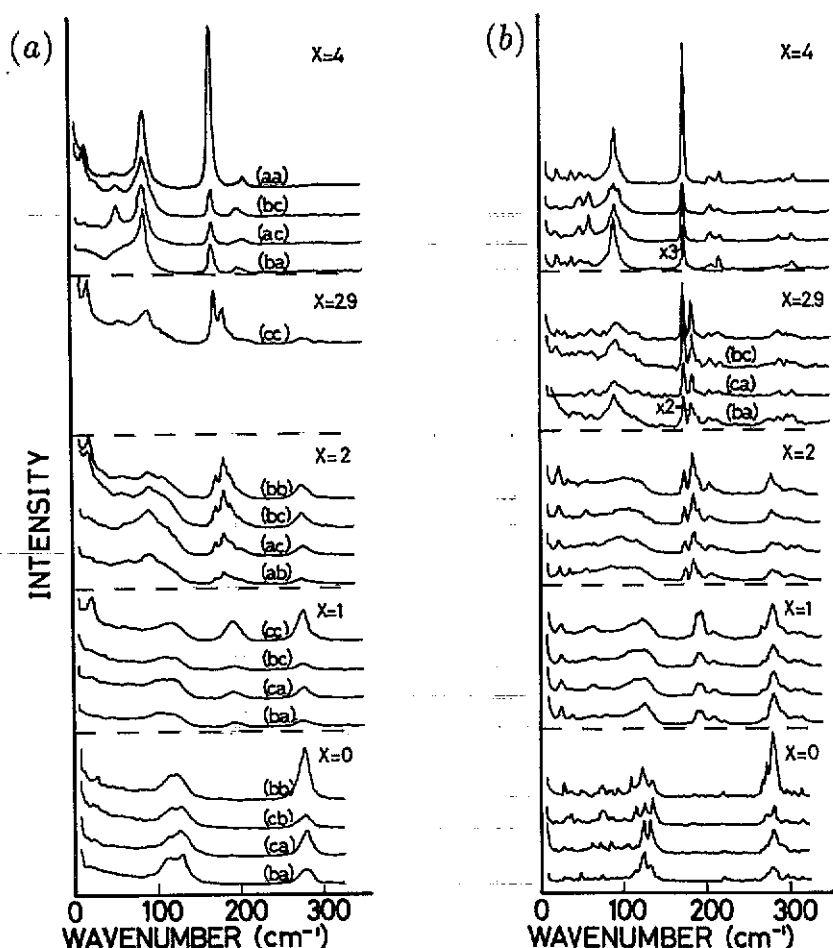


Figure 2. (a) Polarized Raman spectra at  $T = 300$  K of the solid solution TZCB for  $x = 0, 1, 2, 2.9$  and  $4$ . Clearly new modes appear in the spectra of the mixed crystals resulting from the internal modes of the mixed  $\text{ZCB}_n^{2-}$  ions. The scattering geometry is indicated for each curve ((a, b) means incoming polarization along a, polarization of the scattered light along b). The corresponding irreducible representations of the point group can be found in table 2. (b) Polarized Raman spectra at  $T \approx 60$  K of the solid solution TZCB for  $x = 0, 1, 2, 2.9$  and  $4$ . The scattering geometries are the same as in (a). The corresponding irreducible representations can be found in table 3.

of the two non-unique axes becomes elliptical, resulting in a mixing of the scattering polarizations.

In the spectra of the mixed crystals new modes appear due to the mixed character of the  $\text{ZCB}_n^{2-}$  anions. Also some modes shift in frequency as function of the composition and/or the temperature. This is illustrated by the measurement of the lattice mode at  $\sim 24 \text{ cm}^{-1}$  for several temperatures (figure 3(a)) and by the comparison of the frequencies of this mode for different mixing ratios (figure 4).

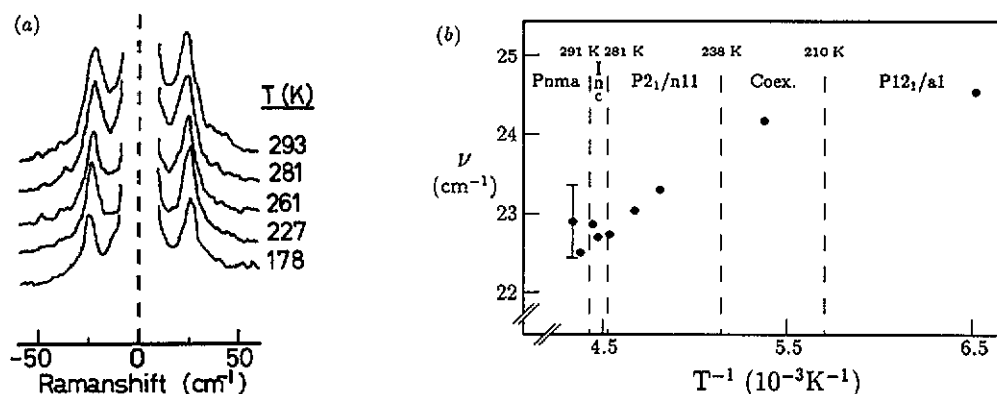


Figure 3. (a) Stokes and anti-Stokes  $A_g$  Raman spectra of the  $\sim 24$   $\text{cm}^{-1}$  mode and the quasi-elastic scattering in TZCB for  $x = 1$  at various temperatures. (b) Temperature dependence of the  $\sim 24$   $\text{cm}^{-1}$  mode in an  $x = 1$  crystal. The mode is insensitive to the phase transition to the incommensurate phase. A hardening of this mode is observed after the phase transition to the monoclinic  $P2_1/n11$  phase.

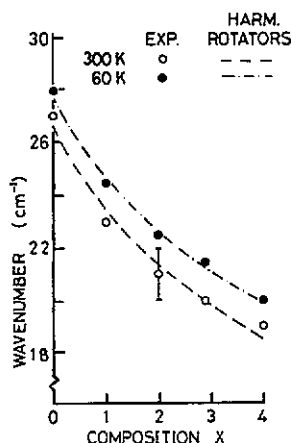


Figure 4. Composition dependence of the  $\sim 24$   $\text{cm}^{-1}$  mode at  $T = 300$  K ( $\bullet$ ) and at  $T = 60$  K ( $\circ$ ). The mode scales with the average mass of the outer atoms of the heavy  $ZCB_n^{2-}$  tetrahedra. This is shown by the broken curves which are fits of the data for a chain of classical harmonic rotators, with frequency  $\nu^2 \sim I^{-1}$  ( $I$  = moment of inertia).

### 3. Raman and IR activity of the $(ZnCl_{4-n}Br_n^{2-})$ modes

Before we turn to the actual activity of the  $ZCB_n^{2-}$  modes, we will first make some remarks on the structure of the TZCB crystals. At room temperature the structure of TZCB is isomorphic for all  $x$ . The space group is  $Pnma$  ( $Z = 4$ ). The unit-cell dimensions change continuously from  $a = 12.268$  Å,  $b = 8.946$  Å and  $c = 15.515$  Å for  $x = 0$  to  $a = 12.681$  Å,  $b = 8.238$  Å and  $c = 16.025$  Å for  $x = 4$  (Arend *et al* 1986). The structure is built up from more or less rigid  $N(CH_3)_4^+$  and  $ZCB_n^{2-}$  tetrahedra positioned at  $(x, \frac{1}{2}, z)$  with site symmetry  $C_s$  in the pure crystals. On lowering the temperature, the TZCB crystals undergo several structural phase transitions, resulting

mainly in rotations ( $\theta_x, 0, \theta_z$ ) and translations ( $0, t_y, 0$ ) of the tetrahedra. Due to the rotations, the site symmetry of the tetrahedra changes from  $C_4$  to  $C_1$  (the mirror plane  $m_y$  is lost). The low-temperature phases have been determined for the  $x = 0$  (Sawada 1978),  $x = 2.2$  (Colla 1987) and  $x = 4$  (Trouelan 1985) compounds. The space groups of the  $x = 0$  and  $x = 4$  compounds are respectively orthorhombic  $P2_12_12_1$  ( $Z = 12$ ,  $T < 161$  K) and monoclinic  $P112_1/a$  ( $Z = 4$ ,  $T < 287$  K). For the mixed crystals we assume that the low-temperature structures are those found in the phase diagram by Colla *et al* (1984), that is  $P12_1/a1$  ( $Z = 8$ ,  $T < 210$  K) for  $x = 1$  and  $x = 2$  crystals, and  $P112_1/a$  ( $Z = 4$ ,  $T < 273$  K) for  $x = 2.9$  crystals.

### 3.1. Free ion approximation

Since we consider the structure as being built up from rigid tetrahedra, we can discriminate between the internal tetrahedra modes and the external vibration modes (including the vibrational and librational modes of the rigid tetrahedra). The validity of this assumption will be considered later, when we discuss the experimental results. We only consider phonons with wavevector  $k = 0$ .

Here we restrict ourselves to a discussion of the internal  $ZCB_n^{2-}$  modes. We first consider the 'free'  $ZCB_n^{2-}$  anions, neglecting the crystal field and the coupling between the ions. The point group of the  $ZCB_n^{2-}$  anions depends on the value of  $n$ . For  $n = 0$  and  $n = 4$  ions the point group is  $T_d$ , for  $n = 1$  and  $n = 3$  ions  $C_{3v}$  and for the  $n = 2$  ions  $C_{2v}$ . In figure 5 the correlation diagram of the vibrational modes for these various point groups is given. Since  $C_{2v}$  is not a subgroup of  $C_{3v}$ , the correlations can not be determined by a direct subduction. Instead, the correlation is found by a projection of the  $C_{3v}$  modes onto the  $C_{2v}$  modes.

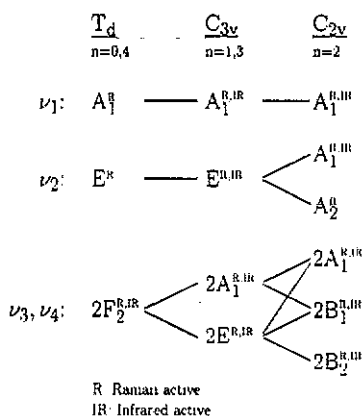


Figure 5. Correlation diagram of the symmetry modes of the free  $ZCB_n^{2-}$  tetrahedra in different compositions. ( $T_d$ :  $n = 0$  or 4,  $C_{3v}$ :  $n = 1$  or 3 and  $C_{2v}$ :  $n = 2$ ).

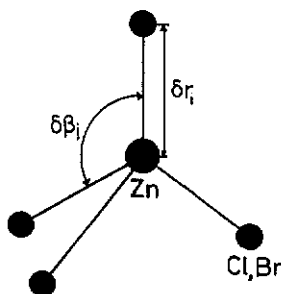


Figure 6. Zn-Y stretching ( $\delta r_i$ ) and Y-Zn-Y bending ( $\delta \beta_i$ ) coordinates in a tetrahedral  $ZnY_4$  ion, where Y stands for Cl, Br.

Figure 5 shows that the degenerate modes in the pure ions split up in the mixed cases. One can gain some more insight into this splitting by considering a simple valence-bond model for the ions, which we discuss briefly now. In this model we

consider the change of mass upon substituting a Cl atom by a Br atom. The valence bond potential is taken to be

$$V = \sum_{i=1}^4 \lambda_i (\delta r_i)^2 + \sum_{j=1}^6 \mu_j (\delta \beta_j)^2$$

where  $\delta r_j$  and  $\delta \beta_j$  are respectively the Zn-Y stretching and Y-Zn-Y bending coordinates (see figure 6). The force constants  $\lambda_i, \mu_j$  are determined from the  $\nu_1$  and  $\nu_2$   $ZCB_n^{2-}$  mode frequencies in the pure compounds using (for  $T_d$  symmetry)

$$\begin{aligned} \nu_1^2 &= \lambda/m & (\text{Zn-Cl, Zn-Br stretching}) \\ \nu_2^2 &= \mu/3m & (\text{Cl-Zn-Cl, Br-Zn-Br bending}) \end{aligned}$$

with  $m$  the mass of either a Cl, or a Br atom. For the Cl-Zn-Br bending force constant a linear interpolation between the two pure cases is used. The resulting force constants are shown in table 1. The model uses only two ( $T_d$  symmetry) or four ( $C_{2v}$  and  $C_{3v}$  symmetry) independent force constants, whereas the actual problem has more (4 for  $T_d$ , 6 for  $C_{3v}$  and 9 for  $C_{2v}$  symmetry). This leads for instance to a higher frequency for the  $\nu_3$  modes of the ions. Despite the restrictions of the model, we think that it gives a clear qualitative picture of the vibrational properties of the heavy tetrahedra. The frequencies of the symmetry modes of the various ions are determined by solving the dynamical matrix of the model. The results of this calculation are shown in figure 7. Three groups of modes are found for the tetrahedra, based on the symmetry modes  $\nu_1, \dots, \nu_4$  of the pure ions. The  $\nu_3$  group at 310–390  $\text{cm}^{-1}$ , the  $\nu_1$  group at 180–280  $\text{cm}^{-1}$  and the  $\nu_2, \nu_4$  group at 80–130  $\text{cm}^{-1}$ . In all groups, the frequency generally decreases as  $n$  is increased, which is expected because of the greater mass of the Br atoms. The splitting of the modes expected from group theory is clearly observed in the model (figure 7). The  $\nu_3$  modes seem to give the best opportunity to measure it because of the relatively large splitting of these modes, whereas the  $\nu_2$  and  $\nu_4$  modes are probably too closely spaced. If TZCB is a true solid solution, then all the different anions  $ZCB_n^{2-}$  will in general be present in the crystals, and all the modes presented in figure 7 are expected to be observable as internal modes in Raman and FIR experiments. We return to this model in the next section, where the results of the Raman and FIR experiments are discussed.

**Table 1.** Force constants used in the valence-bond model, calculated from the frequencies of the  $\nu_1$  and  $\nu_2$  modes in the pure compounds.

Zn-Cl stretching ( $\nu_1=278\text{cm}^{-1}$ )	$\lambda=160 \text{ N/m}$
Zn-Br stretching ( $\nu_1=170\text{cm}^{-1}$ )	$\lambda=136 \text{ N/m}$
Cl-Zn-Cl bending ( $\nu_2=116\text{cm}^{-1}$ )	$\mu=9 \text{ N/m}$
Br-Zn-Br bending ( $\nu_2=56\text{cm}^{-1}$ )	$\mu=5 \text{ N/m}$
Cl-Zn-Br bending	$\mu=7 \text{ N/m}$

### 3.2. Tetrahedral modes in the crystals

We now turn to the activity of the internal  $ZCB_n^{2-}$  modes in the crystals. In table 2 the activities of these modes in the high-temperature  $Pnma$  phase are given. This



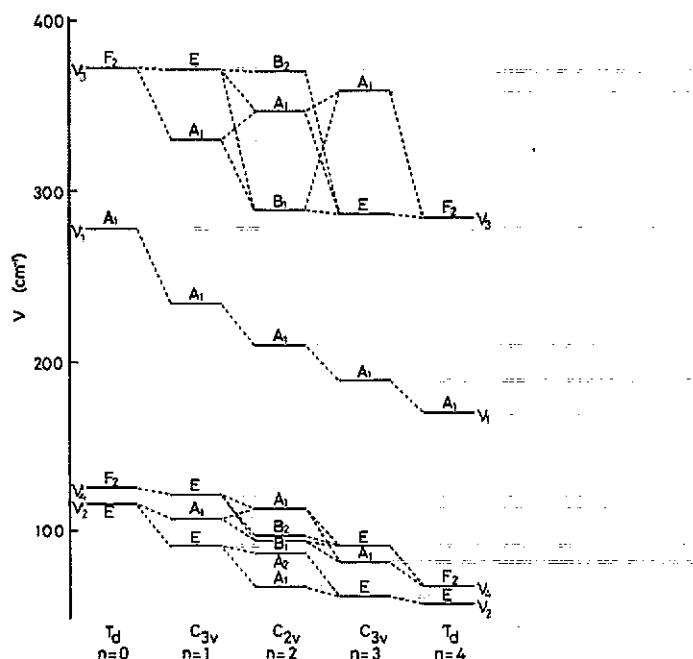


Figure 7. Vibrational energy levels calculated from a valence bond potential model for the various  $ZCB_n^{2-}$  anions. The force constants used, and the characteristic features of this model are discussed in section 3.

table is based on the site symmetry  $C_s$  for the  $ZCB_n^{2-}$  ions. In the mixed crystals however, this mirror symmetry may be lost. This is, in particular, the case when the two atoms which are outside the mirror plane  $m_y$  are of a different kind. In that case the site symmetry is  $C_1$ , and the modes will be active in all geometries (in both Raman and FIR experiments). If the substitution of Cl by Br is totally disordered, the site symmetry will also be  $C_1$ .

Table 2. Raman and infrared activity of the internal  $ZCB_n^{2-}$  modes in the high-temperature  $Pnma$  phase of the TZCB crystals. The site symmetry of the ions is  $C_s$ .

Pnma (Z=4) site symmetry $C_s$				
$D_{2h}$	$\nu_1$	$\nu_2$	$\nu_3 + \nu_4$	activity
$A_g$	1	1	4	(a,a),(b,b),(c,c)
$B_{1g}$	0	1	2	(b,c)
$B_{2g}$	1	1	4	(a,c)
$B_{3g}$	0	1	2	(a,b)
$A_u$	0	1	2	-
$B_{1u}$	1	1	4	a
$B_{2u}$	0	1	2	b
$B_{3u}$	1	1	4	c

The above differences in site symmetry, and thus in selection rules, gives a means to determine whether there is some kind of ordering, leaving the mirror  $m_y$  intact. This is for instance the case if the substitution of Cl by Br preferentially takes place

on the Y site of the tetrahedra with the smallest thermal motions (Colla *et al* 1987), with Zn-Y in the mirror plane, and the bond along *a*.

At low temperatures the site symmetry of the tetrahedra is always  $C_1$ , leading to an activity of all modes in all geometries. However, detectable in the spectra is the number of different frequencies of a given mode, due to the presence of a different number of tetrahedra in the primitive cell of the compounds, and the mixed character of the tetrahedra. The activity of the  $ZCB_n^{2-}$  modes are given in table 3(a) for  $x = 0$ , in table 3(b) for  $x = 1$  and  $x = 2$ , and in table 3(c) for the  $x = 2.9$  and  $x = 4$  compounds.

**Table 3.** Raman and infrared activity of the internal  $ZCB_n^{2-}$  modes in the low-temperature phases of the various TZCB crystals. The site symmetry is  $C_1$  in all cases. (a)  $x = 0$  crystals, space group  $P2_12_12_1$  ( $Z = 12$ ). (b)  $x = 4$  and  $x = 2.9$  crystals, space group  $P112_1/a$  ( $Z = 4$ ). (c)  $x = 1$  and  $x = 2$  crystals, space group  $P12_1/a1$  ( $Z = 8$ ).

a. $P2_12_12_1$ ( $Z=12$ ) site symmetry $C_1$						b. $P112_1/a$ ( $Z=4$ ) site symmetry $C_1$					
$D_2$	$\nu_1$	$\nu_2$	$\nu_3+\nu_4$	activity		$C_{2h}$	$\nu_1$	$\nu_2$	$\nu_3+\nu_4$	activity	
A	3	6	18	(a,a),(b,b),(c,c)		$A_g$	1	2	6	(a,a),(b,b),(c,c),(a,b)	
$B_1$	3	6	18	a,(b,c)		$B_g$	1	2	6	(a,c),(b,c)	
$B_2$	3	6	18	b,(a,c)		$A_u$	1	2	6	c	
$B_3$	3	6	18	c,(a,b)		$B_u$	1	2	6	a,b	

c. $P12_1/a1$ ( $Z=8$ ) site symmetry $C_1$					
$C_{2h}$	$\nu_1$	$\nu_2$	$\nu_3+\nu_4$	activity	
$A_g$	2	4	12	(a,a),(b,b),(c,c),(a,c)	
$B_g$	2	4	12	(a,b),(b,c)	
$A_u$	2	4	12	b	
$B_u$	2	4	12	a,c	

#### 4. Interpretation of the spectra

In the first part of this section the FIR and Raman spectra presented in section 2 are discussed in terms of the internal modes of the  $ZCB_n^{2-}$  ions. A discussion of the external modes will be given in the second part of this section.

##### 4.1. Internal $(ZnCl_{4-n}Br_n)^{2-}$ modes

**4.1.1. FIR spectra.** Three broad absorption bands are observed in the FIR spectra of the pure compounds, of which two are assigned to the  $\nu_3$  and  $\nu_4$  internal  $ZCB_n^{2-}$  modes (see figure 1). For the pure Cl compound the absorption maxima of these modes are found at approximately  $\nu_3 = 275 \text{ cm}^{-1}$  and  $\nu_4 = 130 \text{ cm}^{-1}$ , for the Br compound the frequencies are respectively  $200 \text{ cm}^{-1}$  and  $90 \text{ cm}^{-1}$ .

The low-frequency absorption band in the spectra is assigned to the external vibrational modes. Due to the weak coupling to the lattice of the internal modes, the tetrahedral symmetry of the ions is almost conserved. Hence, the  $\nu_1$  and  $\nu_2$  modes are expected to be only weakly absorbing in FIR experiments. In the pure compounds, the  $\nu_2$  modes are not observed. In the Cl compound this results from the (near) degeneracy of these modes with the  $\nu_4$  modes, whereas in the Br compound the  $\nu_2$  modes coincide with the external modes.

The frequencies of the fully symmetric  $\nu_1$  modes nearly coincide with those of the  $\nu_3$  modes, and are not observed in the spectra. The spectra of the mixed crystals show absorbing bands at the  $\nu_3$  frequencies for both pure compounds. These bands result from the  $\nu_3$  modes of the pure ions, as well as from the ions with a mixed character. This can be concluded from the valence-bond model (figure 7) and the relative strong intensity of the  $200\text{ cm}^{-1}$  band in the  $x = 1$ , and the  $278\text{ cm}^{-1}$  band in the  $x = 2.9$  spectra.

The  $\nu_4$  absorption band shifts toward lower frequency as  $x$  increases, consistent with the valence-bond model. In the spectrum of the  $x = 2.9$  compound two absorption dips are observed at  $92\text{ cm}^{-1}$  and  $109\text{ cm}^{-1}$ . The structure at  $92\text{ cm}^{-1}$  is mainly due to the  $\nu_3$  modes of the  $\text{ZnBr}_4^{2-}$  ions. As will be shown later on, the ions with a mixed character present in the  $x = 2.9$  crystals are mainly the  $\text{ZnClBr}_3^{2-}$  ions. We therefore assign the structure at  $109\text{ cm}^{-1}$  to the  $\nu_3$  internal modes of the  $\text{ZnClBr}_3^{2-}$  ions.

**4.1.2. Raman spectra of the pure compounds.** Before we turn to the spectra of the mixed crystals, we will first examine the spectra of the pure compounds, starting with the  $x = 4$  compound. In the high-temperature Raman  $A_g$  spectrum (figure 2(a), upper curve), the four internal modes of the  $\text{ZnBr}_4^{2-}$  anions are all clearly observed as more or less sharp peaks in the spectrum. In table 4 we have compared the frequencies of these modes with the frequencies measured for the anions in an aqueous solution (Morris *et al* 1963). Since there are only slight differences between these two, we can conclude that the effects of the crystal field on the intra-molecular forces in  $\text{ZnBr}_4^{2-}$  are fairly small. This can also be concluded from the small FWHM (full width at half maximum) of the modes, which indicates only a small splitting of the modes due to the crystal field. In the  $x = 4$  Raman  $B_{1g}$ ,  $B_{2g}$  and  $B_{3g}$  spectra at 300 K (figure 2(a)) we again observe all the internal  $\text{ZnBr}_4^{2-}$  modes. For the  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  modes this is expected from the selection rules (table 2). The  $\nu_1$  mode, however, should be inactive in  $B_{1g}$  and  $B_{3g}$  symmetry. The fact that in these cases also a non-zero intensity is found is probably due to the large degree of rotational freedom (Colla 1987) of the  $\text{ZnBr}_4^{2-}$  tetrahedra around the  $a$ - and  $c$ -axis, effectively lowering the site symmetry from  $C_4$  to  $C_1$ .

Table 4. Comparison of the frequencies of the internal  $\text{ZnBr}_4^{2-}$  and  $\text{ZnCl}_4^{2-}$  modes measured by Raman spectroscopy for the crystals with the corresponding frequencies for the ions in an aqueous solution (Morris 1963).

	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$
$\text{ZnCl}_4^{2-}/\text{H}_2\text{O}$	275	79	306	104
$[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$	278	116	275*	127
$\text{ZnBr}_4^{2-}/\text{H}_2\text{O}$	172	66	208	88
$[\text{N}(\text{CH}_3)_4]_2\text{ZnBr}_4$	170	56	210	88

\* From the FIR data.

In the  $x = 4$  low-temperature spectra (figure 2(b)), all modes are active in all geometries, consistent with the selection rules (table 3(c)). A single  $\nu_1$  mode is observed in all geometries and the six different  $\nu_3$  and  $\nu_4$  modes are better resolved. It is not clear whether the  $\nu_2$  modes (2 in each geometry) are resolved due to the coincidence with the external modes.

For the  $x = 0$  compound there are some degeneracies which blur the above picture a bit. The  $\nu_2$  and  $\nu_4$  modes are strongly overlapping and the  $\nu_1$  modes are (nearly) degenerate with the  $\nu_3$  modes. The latter can be concluded from a comparison of  $\nu_1$  modes in the Raman spectra (figure 2(a) and 2(b), lower curves) with the  $\nu_3$  modes in the FIR spectrum (figure 4, lower curve). The comparison of the observed frequencies of the  $ZnCl_4^{2-}$  internal modes with those of the ions in an aqueous solution (Morris *et al* 1963) in table 4 shows that in this case the differences are rather large, indicating a non-negligible effect of the crystal field on the intra-molecular forces. This makes the subdivision into external and internal modes in this compound questionable.

In the high-temperature Raman spectra (figure 2(a)) again a non-zero intensity is found in the  $\nu_1$  region in all geometries. Indeed, part of the intensity in the  $B_{1g}$  and  $B_{3g}$  spectra can be explained by the activity of the  $\nu_3$  mode, as proposed by Meekes *et al* (1988). The large intensity in these geometries indicates, however, that it is also partly due to the activity of the  $\nu_1$  modes, again resulting from the large thermal factors of the  $ZnCl_4^{2-}$  anions.

In the  $x = 0$  low-temperature spectra (figure 2(b)) the different modes are as expected active in all geometries. The  $\nu_1$  mode is split up into several peaks, reflecting the larger number of formula units in the unit cell in this case (see also table 3(a)). It is not clear whether part of the structure in the  $\nu_1$  region results from the (weak) activity of the  $\nu_3$  modes.

**4.1.3. Raman spectra of the mixed compounds.** We now turn to the spectra of the mixed crystals. In the Raman spectra (figure 2(a) and 2(b)) additional peaks appear in the spectra, which are not observed in the spectra of the pure compounds. This is clearest in the region of  $\nu_1$ ,  $\nu_3$  modes ( $150\text{--}350\text{ cm}^{-1}$ ). These extra modes are due to the presence of mixed  $(ZnCl_{4-n}Br_n)^{2-}$  ions in the crystals, indicating that the compounds are true solid solutions, and not just a mixture of the two pure crystals. The peaks in the  $\nu_1$ ,  $\nu_3$  region of the  $A_g$  Raman spectra at  $T = 300\text{ K}$  (figure 2(a)) are fitted to Lorentzian shaped modes. The results of these fits can be found in table 5. The additional modes observed in the  $\nu_1$ ,  $\nu_3$  region are assigned to the  $\nu_1$  modes (neglecting the  $\nu_3$  modes, which generally have a low intensity) of respectively the  $ZnCl_3Br^{2-}$  ion ( $183\text{ cm}^{-1}$ ), the  $ZnCl_2Br_2^{2-}$  ion ( $191\text{ cm}^{-1}$ ) and the  $ZnClBr_3^{2-}$  ion ( $202\text{ cm}^{-1}$ ), based on the qualitative model presented earlier and the results obtained by Delwaulle (1955) for the mixed anions in an aqueous solution. The FWHM of these  $\nu_1$  modes increases as the number of Cl atoms in the ion increases (see figure 8), indicating that the ions become more sensitive to the crystal field. This is possibly connected to the large number of phases found for low  $x$  values (the anharmonicity of the potential increases as  $x$  decreases).

Table 5. Frequencies and relative intensities resulting from fits of the  $\nu_1$  modes in the  $A_g$  Raman spectra at  $T = 300\text{ K}$  to Lorentzian shaped peaks.

x=0		x=1		x=2		x=2.9		x=4	
$\nu$ ( $\text{cm}^{-1}$ )	$I_0$	$\nu$ ( $\text{cm}^{-1}$ )	$I_0$	$\nu$ ( $\text{cm}^{-1}$ )	$I_0$	$\nu$ ( $\text{cm}^{-1}$ )	$I_0$	$\nu$ ( $\text{cm}^{-1}$ )	$I_0$
		184	9.7	173	13.1	171	43.0	170	93.4
		192	28.1	183	33.0	182	35.9		
		202	7.6	191	17.8	192	4.0		
				202	7.4	205	6.4	210	6.6
278	100	276	54.6	276	28.7	280	10.6		

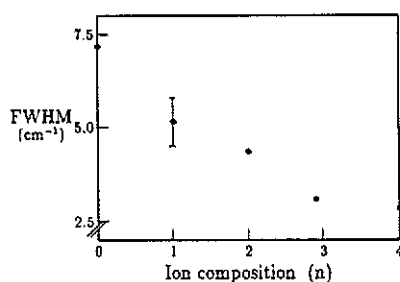


Figure 8. Ion composition ( $n$ ) dependence for the  $\text{ZCB}_n^{2-}$  ions of the FWHM of the  $\nu_1$  modes in the Raman  $A_g$  high-temperature spectra as determined from the Lorentz fits presented in table 5.

Using the intensities listed in table 5, an estimate can be made of the relative concentrations  $\rho_n(x)$  of the various  $\text{ZCB}_n^{2-}$  anions in the different TZCB crystals, which in turn can be used to estimate the value of  $x$ . In order to do this, we assume that the intensity of the peaks is only proportional to the concentration of scatterers in the crystal, and therefore one has an equal scattering efficiency for the various  $\text{ZCB}_n^{2-}$  anions. A problem arises for the  $\text{ZnCl}_3\text{Br}^{2-}$  ion, because the  $\nu_1$  mode of this ion is (almost) degenerate with the  $\nu_3$  modes of the  $\text{ZnBr}_4^{2-}$  ion. The influence of the  $\nu_3$  modes can be estimated using the intensity ratio  $I_0(\nu_3)/I_0(\nu_1)$  of  $\text{ZnBr}_4^{2-}$  in the spectra of the  $x = 4$  compound and the intensity  $I_0(\nu_1)$  of  $\text{ZnBr}_4^{2-}$  in the spectra of the mixed crystals. The estimated values of  $\rho_n(x)$  are listed in table 6. This table shows that the  $\text{ZnCl}_3\text{Br}^{2-}$  anion is only present in very low concentrations in the mixed crystals. From the Raman results of Benhmida *et al* (1987) we conclude that the concentration of this ion is only appreciable for very low values of  $x$ . It seems that there is a preference to form either the pure anions or mixed ions with more than one Br atom. Table 6 also shows the calculated values  $x_{\text{calc}}$  of the composition of the crystals. These values lie within 10% of those of the growth solutions, which is a fair agreement in view of the method used to obtain  $x_{\text{calc}}$ .

Table 6. Relative concentrations  $\rho_n(x)$  of the various configurations of the mixed tetrahedra in crystals with different composition ( $x$ ), calculated from the fitted intensities presented in table 4. From these concentrations the crystal composition  $x_{\text{calc}}$  has been calculated.

$n$	$x$				
	0	1	2	2.9	4
0	100	54.7	28.9	11.0	0
1	0	7.5	6.6	3.5	0
2	0	28.1	18.0	4.1	0
3	0	9.7	33.3	37.0	0
4	0	0	13.2	44.4	100
$x_{\text{calc}}$	0	0.93	1.95	3.00	4

Until now we have been discussing mainly the  $\nu_1$  modes of the mixed ions in the Raman high-temperature  $A_g$  spectra. The other modes of the mixed ions are not directly observed in the Raman spectra. For the  $\nu_3$  modes this is due to their near degeneracy with the  $\nu_1$  modes of the tetrahedra. In the FIR spectra we observed two bands in the  $\nu_1, \nu_3$  region, originating mainly from the  $\nu_3$  modes. In our model

(figure 7) the  $\nu_3$  frequencies are generally too high. Qualitatively, however, the model predicts two groups of  $\nu_3$  modes for the mixed crystals, approximately at the  $\nu_3$  frequencies of the pure ions, as is also observed in the FIR spectra.

The  $\nu_2$  and  $\nu_4$  modes generally overlap with each other, and with the external modes in both the Raman and FIR spectra. In the mixed crystals the  $\nu_2$  and  $\nu_4$  structure is broadened due to the splitting of the modes, and it shifts towards lower frequency as  $x$  increases (see also figure 7). Using the polarized Raman spectra and the selection rules of the  $\nu_1$  modes in the  $Pnma$  phase of the mixed crystals, one can in principle determine whether the site symmetry of the ions is  $C_s$  or  $C_1$ , and thus obtain some insight in a possible ordering of the substitution of Cl by Br (see section 3). Unfortunately, the large thermal factors of the ions already effectively lowers the site symmetry to  $C_1$  in the pure compounds, as it follows from the  $\nu_1$  presence in the  $B_{1g}$  and  $B_{3g}$  spectra. Therefore the site symmetry of the ions in the mixed crystals is also expected to be  $C_1$ , regardless of any ordering in the substitution.

#### 4.2. External modes

In the high-temperature FIR and Raman spectra the external modes are observed as broad structures at low frequencies. The only resolved peak is found at  $\sim 24\text{ cm}^{-1}$  in the Raman spectra (see figures 2(a) and 3). The composition dependence of this mode (see figure 4) suggests that it is a librational mode of the  $ZCB_n^{2-}$  ions. This is shown by the dashed curves in figure 4, which give the  $k = 0$  frequency dependence of a chain of harmonically coupled rotators with the same moments of inertia as an average  $ZCB_n^{2-}$  ion in the corresponding crystal. On the other hand, the pure librational modes of the crystals in the  $Pnma$  phase are expected to be only Raman active in either  $A_g$  and  $B_{2g}$  or  $B_{1g}$  and  $B_{3g}$  geometry, whereas figure 2(a) shows that this mode is mainly active in  $A_g$  and  $B_{1g}$  geometry. Figure 3 shows the temperature dependence of this mode in a  $x = 1$  compound. The mode is insensitive to the phase transition to the incommensurate phase at  $T_i \approx 291\text{ K}$ , which is mainly a modulated rotation of the heavy tetrahedra around the  $b$ -axis. After the transition to the monoclinic  $P2_1/n11$  phase at  $T_m = 282\text{ K}$  a hardening of the mode is observed.

Another interesting feature in the high-temperature Raman spectra is the broadening of the Rayleigh wings observed predominantly in the  $A_g$  and  $B_{1g}$  spectra. The temperature dependence in figure 3(a) shows that this broadening decreases as the temperature decreases. Indeed, in the low-temperature spectra (figure 2(b)) this broadening has disappeared. This broadening possibly results from quasi elastic scattering from the  $N(CH_3)_4^+$  ions due to the large rotational freedom of these ions at higher temperatures (Pauling 1930, Frenkel 1935). At low temperatures this freedom freezes out (Blinic 1979).

#### 5. Conclusions

We have presented polarized Raman spectra and FIR transmission spectra of the solid solution  $(N(CH_3)_4)_2ZnCl_{4-x}Br_x$  for  $x = 0, 1, 2, 2.9$  and  $4$  at  $T \approx 60\text{ K}$  and  $T \approx 300\text{ K}$ . In the spectra new modes appear, which are not present in the spectra of the pure Cl and Br crystals. These modes are assigned to the internal modes of the  $ZCB_n^{2-}$  ions, in agreement with a simple valence-bond model. The thermal motions of the heavy tetrahedra effectively lower the site symmetry in the high-temperature phase from  $C_s$  to  $C_1$ . It is therefore not possible to determine from the selection rules whether there

are preferred ion sites for the substitution of Cl by Br. The appearance of all the  $\nu_1$  mixed ion modes in the spectra indicate, however, that there are no preferred sites for the substitution.

The most interesting features in the spectra for further investigation are the  $\sim 24\text{ cm}^{-1}$  mode of the  $\text{ZCB}_n^{2-}$  ions, which given its temperature dependence (hardening in the lock-in phase) could be coupled to the soft mode which is responsible for the incommensurate phase. Another interesting feature is the broadening of the Rayleigh wing, possibly caused by quasi-elastic light scattering from the  $\text{N}(\text{CH}_3)_4^+$  ions. This broadening is expected to change discontinuously at the various phase transitions of the crystals. From the temperature and composition dependence of these modes one can gain some more insight into the mechanisms of the phase transitions in this system.

### Acknowledgments

We would like to express our thanks to Dr H Meekes and Dr Th Rasing for valuable discussions on the subject, and Professor H van Kempen for his support. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM).

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